Supporting Information:

Predicted Structures of the Active Sites Responsible for the Improved Reduction of Carbon Dioxide by Gold Nanoparticles

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simulation methods

We used LAMMPS (1 Feb 2014 version)\textsuperscript{1} with the USER-REAXC package and fix 
\texttt{qeq/reax}.\textsuperscript{2} for the Molecular Mechanics (MM) Dynamics simulations. A Nose-Hoover 
thermostat was used to control the temperature with a damping parameter of 100 time steps.

To grow a gold (Au) nanoparticle (NP), we used a zigzag carbon nanotube (CNT) with a 
diameter of 8.39 nm as the catalysis support, which was kept fixed during all the simulations. The Embedded-atom-model (EAM) \textsuperscript{3} was used to describe the interaction between Au atoms, 
and a Lennard-Jones (LJ) potential was used to describe the interaction between Au and the 
CNT. The temperature for the growth simulation was 300K, and the deposition rate for the 
growth simulation was 3.0 Å ns\textsuperscript{-1}. The time step was 1 fs. After 35 ns of growth simulation, an 
Au NP with a normal thickness of about 10 nm was obtained on the CNT support. Annealing 
simulations were carried out to heal the defect and increase the grain size. Each annealing cycle 
included 10 ps cook-off simulation from 300 K to 1200 K, 5 ps NVT simulation at 1,164 K, 10 
ps annealing from 1,164 K to 300 K and 15 ps NVT simulation at 300 K. After 120 annealing 
cycles, a fully crystallized Au NP formed on CNT support. In the annealing trajectory, the Au-
NP structure after 63 annealing cycles is mostly close to the experimental structure, which was 
further refined by using 20 ps ReaxFF reactive force field (ReaxFF) simulation at 300K using a 
previous published Cu-C ReaxFF parameters.\textsuperscript{4} The time step for the reactive force field 
(ReaxFF) simulations was 0.25 fs.

Quantum mechanics calculations were performed with VASP package\textsuperscript{5-7}, using the PBE 
flavor\textsuperscript{8} of DFT and the projector augmented wave (PAW) method\textsuperscript{9} to account for core-valence 
interactions. The kinetic energy cutoff for plane wave expansions was set to 400 eV. The 
Methfessel-Paxton smearing of second order with a width of 0.2 eV was applied. The 
convergence criteria are $1 \times 10^{-5}$ eV energy differences for solving the electronic wave function. 
All geometries (atomic coordinates) are converged to $1 \times 10^{-2}$ eV/Å for maximal components of 
forces.

Cluster models for VASP calculations were cut from the simulated nanoparticle using a 
cut-off of 8 Å taking the selected site as a center. We consider that this provides an accuracy 0.02 
eV while keeping the computational cost modest. For cluster calculations, a 20 Å cubic box was 
used, and only gamma point was considered in these calculations. All the Au atoms were fixed in 
cluster calculations.

Debyer, (freely available on \url{https://github.com/wojdyr/debyer}), was used to calculate the 
diffraction pattern for the synchrotron x-ray source. QSTEM (freely available on 
\url{http://qstem.org/}) was used to simulate the TEM images.
The simulated XRD-diffraction pattern of Au NP shows peaks of FCC Au. The widened peak of Au NP is due to the Nano-size effect.
Figure S2. Comparison of the equation of state of FCC Au between ReaxFF and QM.
Figure S3. Au octahedral with a length of 6.93 nm (10,425 Au atoms), which consists of 2,024 facet sites (87.77%), 276 edge sites (11.97%) and six corner sites (0.26%).
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<th>Nr of atoms; cov.r; valency;a.m;Rvdw;Evdw;gammaEEM;cov.r2;# alfa;gammadw;valency;Eunder;Eover;chiEEM;etaEEM;n.u. cov r3;Elp;Heat inc.;n.u.;n.u.;n.u.;n.u. ov/un;val1;n.u.;val3, val4</th>
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**Context:** The table contains various numerical data related to bond energies, dispersions, and other physical properties. The entries are formatted in a way that suggests they are results from computational chemistry calculations, possibly involving molecular structures or materials properties.
References


